PRESSURE DEPENDENCE OF THE ELECTRICAL CONDUCTANCE OF PRESSED CASSITERITE POWDERS

S. C. MITRA* AND B. U. OKONJI

UNIVERSITY OF NIGERIA, NSUKKA.

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ABSTRACT. Pressure dependence of the electrical conductance of cassiterite powder has been investigated at room temperature and low compression, up to pressure of $90 kg/cm^2$. The conductance is found to increase with pressure exponentially according to the equation $G = A \exp(Kp_m)$. A model based on elastic properties and surface charge layers of the grains is developed to qualitatively explain the results.

INTRODUCTION

Whilst a fairly large amount of work has been done on the pressure dependence of conductance of powdered metals, similar works on semiconducting powders have been somewhat limited.

The pioneer work of Kantorovicz (1931) on metal powders shows that the electrical conductance G varies according to eqn (1)

$$G = C_1 p_m^{\frac{1}{2}} + C_2 \qquad \ldots (1)$$

where p_m is the pressure and C_1 and C_2 are constants depending on the elastic properties of the metal.

Holm (1958) has given a theoretical basis of eqn (1) showing that on the basis of constriction resistances arising out of the narrow highly resistive points of contact of the grains through which the current flows, the conductivity of pressed metal powders satisfies eqn (2)

$$G = C \left(\frac{p_m}{H} \right)^k + f(p_m) \qquad \ldots (2)$$

where H is the hardness factor and C and $f(p_m)$ are functions of the elastic properties of the material; K is a constant such that ordinarily $\frac{1}{2} < K < 1$; for clean contact surface K is equal to $\frac{1}{2}$.

The earliest works on pressure dependence of resistance of semiconducting powders were on aluminium oxide and zinc oxide by Davis (1950), and by Brentanno and Davis (1951). They find that in a general way the conductance of powders

* Present address—Defence Laboratory, Jodhpur.

increases with pressure. Bridgmann (1951) measured the resistance of semiconducting powders in the high compression range up to 50,000 kg/cm^2 hydrostatic pressure and finds that in the case of zinc oxide the resistance decreases with increasing pressure both at 25°*C* and 100°C *but* decreases with decrease of pressure at 200°*C*.

The investigations of Davis were followed up by Brentanno and Goldberg (1954). They applied unidirectional stress up to 38,000 lb/in^2 over a range of temperatures and conrm the general findings of Davis. They, however, find that with pressure variation the conductance attains a maxima and for lower temperature the maxima is obtained at lower pressure.

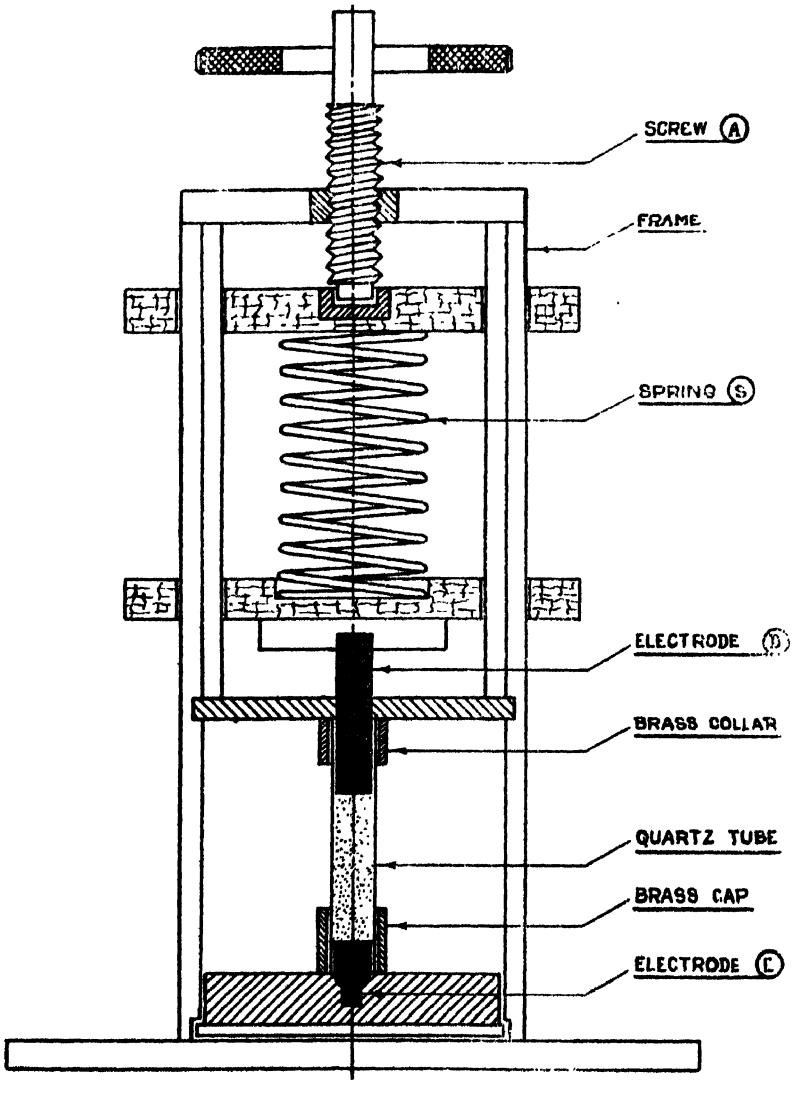

Fig. 1. Schematic Diagram of the Compressor.

Works hitherto on the conductance of semiconducting powders had been confined in interest to high compression range. The present work is a study of what happens to a semiconducting powder when subjected to low compression.

EXPERIMENTAL

Electrical resistance of pressed cassiterite powder at different undirectional pressure was measured in an ambient of air at room temperature. The apparatus used is shown in fig. 1.

The powder is contained in a quartz tube mounted vertically on a brass cap containing the lower electrode E. Pressure is applied by means of a screw A, acting through the intermediary of a calibrated spring S to the second electrode D. Resistance was measured by conventional method.

Readings of conductance were taken at an interval of 17.7 kgm/cm^2 up to 88.4 kgm/cm^2 during increase and decrease of pressure.

RESULTS

Measurements have been made on three samples S_1, S_2 and S_3 of lengths 3.37, 4.6, and 4.7 cms respectively and 2.83 sq. cm. cross sectional area.

Pressure dependence of conductance is plotted as logarithm of conductance Vs pressure (fig. 2). The curve is linear and satisfies equation

$$G = A \exp(Kp_m) \qquad \ldots (3)$$

where G = Conductance and p = pressure at the electrode.

A and K are constants which varies slightly from specimen to specimen

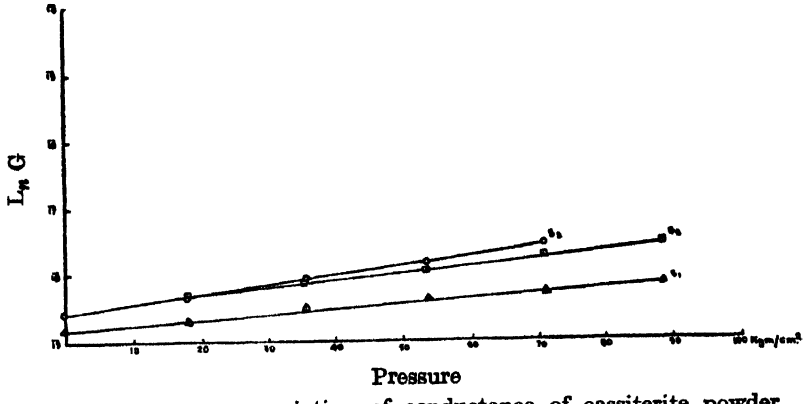

Fig. 2. Pressure variation of conductance of cassiterite powder.

INTERPRETATION OF EXPERIMENTAL RESULTS

Powdered materials consist of an agglomeration of grains with interstices and grain boundaries. In the case of powdered metal the flow of current is

channelised only through microscopic contact spots which accounts for the high resistance of metal powders (Holm 1958). The contact areas may be fully or partially conducting, in the latter case due to overlying multimolecular gas films. With increased pressure the conducting contact areas enlarge, due to elastic or plastic deformations of the grains as well as due to the elimination of the disturbing films. The electrical conductance of metal powder is thus a function of pressure, as well as of the geometrical and mechanical properties of the grains and resistivity of the material.

In semiconducting powders the above picture is modified due to the presence of surface charge on the grains (Hannay 1960). The individual crystallites are generally covered by a layer of charge at the surface. The electrical properties of the surface layers are significantly different from those of the interior. The surface layer may be either the exhaustion or enriched type. In the former case, the surface has reduced conductivity than the bulk and in the latter case opposite. Under pressure, at the points of contacts of the grains, some quasi-sintering will take place as a result of which the grains will be inter-connected by necks, whose diameters are comparable with the depth of the space charge layer. The carrier concentration at the neck will be different from that of the bulk. Consequently, the position of the Fermi level at and away from the neck will be different, thereby modifying the energy band structure. The conductance of the necks will be predominant in the overall conductance of the samples. Pressure will change the nature and size of the interconnecting necks and hence change conductance of the sample. So far, it has been assumed that the interstices are perfect insulators. At high temperatures and if the materials have low work function the pores may also become conducting due to election gas present in the pores as a result of thermionic emission as has been observed in Barium oxide and Barium Strontium oxide by Loosjes and Vink (1949).

We propose to explain the results of our investigations on the basis of the foregoing discussion. We assume that for our material, on account of investigations at room temperature and low pressures neither pore conductance nor variation of forbidden energy gap with pressure apply (Bridgmann 1951, 1953, Bardeen 1949, Taylor 1950; Paul and Brooks 1954; Bretanno and Goldberg 1954).

For powder samples, when a force F is applied on the electrode of cross sectional area A_m, the pressure p on the particle contact area a is not the same as the pressure p_m on the electrode. This is obviously on account of the interstices present in the bulk of the powder. The particle contact area a is the sum of the contact areas for any cross section of the powder and represents the average pressure over the particle cross sectional area a. Neither p nor a is measurable but they are related to the macroscopic measurable quantities p_m and A_m by eqn (4)

$$F = p_m A_m = pa \qquad \ldots (4)$$

Following Holm (1958), the actual contact area increases with pressure up to a limit. The increase is large at low pressures and very small at high pressures. We assume that in the low pressure range, da/dp_m is constant in the first order.

For the semiconductor specimen under consideration, we represent conductance G by the following classical expression.

$$G = G' \exp\left(-\frac{E}{KT}\right) \qquad \ldots (5)$$

This expression is valid for $E << KT$ where E is the conductivity activation energy. This is true for cassiterite since its conductivity activation energy is greater than 0.5 e.v. (Kohnke 1962, Mitra 1967). G depends on the physical parameters of the sample including the geometry of the interconnecting necks. From (5)

$$L_n G = L_n G' - \frac{E}{2KT} \qquad \ldots (6)$$

We assume that G' and E are dependent on pressure only since the temperature is constant and can be represented by (7)

$$\left.\begin{aligned} G' &= G_0 + \frac{\partial G'}{\partial p_m} \cdot p_m \\ E &= E_0 + \frac{\partial E}{\partial p_m} \cdot p_m \end{aligned}\right\} \qquad \ldots (7)$$

From (6) and (7)

$$L_n G = \text{const} + \left(\frac{1}{G_0}\frac{\partial G'}{\partial p_m} - \frac{1}{2KT}\frac{\partial E}{\partial p_m}\right) p_m \qquad \ldots (8)$$

Analysis of our data shows that Holm's theory of constriction resistance for metal powder alone is inadequate to satisfy the experimental findings, which is understandable. Equation (8) agrees with eqn (3) if we assume that the expression within the bracket is a positive constant equal to K of eqn (3) where K is seen from the graph to vary slightly from specimen to specimen. Brentanno and Goldberg's results are in the high compression range and at pressures above conductance maxima, and hence beyond scope of comparison with our findings. In their range of pressure, logarithm of conductance decreases directly with pressure and the constant of proportionality is proportional to p_m and inversely proportional to the critical pressure P_m at which bruising or cracking of particles occurs. This

can be obtained from eqn (8) since at high pressure G' is constant and hence the first term within the bracket in eqn (8) vanishes.

It has not been possible with our present knowledge of surface and bulk effects to untangle the contributions of the respective components of eqn (8). A good deal of expertise will however, be needed before that is possible. Work is in progress along the line and will be reported in due course.

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